REMARKS/ARGUMENTS

Reconsideration of this application in light of the following comments is courteously solicited.

Applicant attaches hereto a paper entitled "Behaviour of Metals in Nitric Acid" received January 19, 1944. This document was previously attached to Applicants' Preliminary amendment of March 13, 2007.

It is submitted that the examiner's rejection of the claims should be withdrawn for the reasons set forth hereinbelow.

Specific reference is made to the final rejection, Applicants' subsequent Request for Reconsideration, and the examiner's Advisory action of October 26, 2006. In that Advisory action the examiner sets forth the following:

> 1) "Applicant's argument regarding the presence of nitrous acid in the coating solution of Bengston in view of Tomlinson and the supporting document "The Conditions of Chemical Change Between Nitric Acid and Certain Metals" (Chemical Abstract) are not convincing since the Chemical Abstract document appears to be directed to CERTAIN metals such as copper, mercury, and bismuth rather than the magnesium metal as disclosed by Bengston in view of Tomlinson. Furthermore, the concentration of nitric acid as disclosed by the Chemical Abstract is also an important factor in the formation of nitrous acid. There are also conditions under which nitrous acid is destroyed as fast as it is generated. The examiner cannot draw the conclusion that the coating solution of Bengston in view of Tomlinson contains nitrous acid directly from the disclosure of the Chemical Abstract. Therefore, the examiner does not find applicant's arguments based on the teachings of the Chemical Abstract persuasive."

In response to the Examiner's comments Applicant submits herewith as Exhibit I a paper from January 1944 entitled Behaviors of Metals in Nitric Acid. This paper describes in detail the

cathodic reduction sequence of nitric acid which involves the generation of nitrous acid. This reduction sequence is an intrinsic behavior of nitric acid and, as can be seeds from the Evans paper, is independent of the metal oxidation talking place. Therefore, the formation of nitrous acid would occur with the magnesium metal disclosed by Bengston in view of Tomlinson. With regard to the destruction issue, Evans is clear that nitrous acid is a byproduct which would result from the cathodic reduction sequence for nitric acid. Applicants believe that the Evens article clearly addresses the examiner's point as quoted above.

In light of the foregoing, Applicant respectfully submits that the claims as pending patentably define over the art of record and an early indication of same is respectfully requested.

An earnest and thorough attempt has been made by the undersigned to resolve the outstanding issues in this case and place same in condition for allowance. If the Examiner has any questions or feels that a telephone or personal interview would be helpful in resolving any outstanding issues which remain in this application after consideration of this amendment, the Examiner is courteously invited to telephone the undersigned and the same would be gratefully appreciated.

It is submitted that the claims as amended herein patentably define over the art relied on by the Examiner and early allowance of same is courteously solicited.

If any fees are required in connection with this case, it is respectfully requested that they be charged to Deposit Account No. 02-0184.
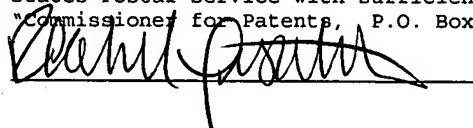
Respectfully submitted,

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Date: May 18, 2007

I, Rachel Piscitelli, hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: "Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313" on May 18, 2007.

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BEHAVIOUR OF METALS IN NITRIC ACID

By U. R. Evans.

It is commonly believed that the behaviour of metals towards nitric acid is a very complex subject. The object of this paper is to show that, by bringing together the results of recent experimental work, the principal facts can be explained simply, naturally, and without any *ad hoc* assumption. No attempt is made to restate the whole of the facts, since good reviews of the situation have been provided by Bancroft[1] and Milligan.[2]

[1] Bancroft, *J. Physic. Chem.*, 1924, 28, 475, 973. [2] Milligan, *ibid.*, 544.

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The formidable equations found in textbooks such as

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$
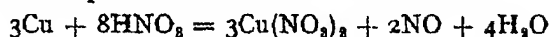
represent at best final results obtained under a limited range of conditions. No one really pictures a collision between eleven molecules. Clearly the individual steps of the mechanism must be much simpler.

It is always legitimate to separate a corrosion reaction into an anodic operation representing the passage of metallic ions into the solution, and a cathodic operation representing the reduction of the reagent, provided that it is remembered that the two changes may often occur at the same point ;[3] there is experimental evidence of spatial separation of the two operations upon discrete anodic and cathodic areas in some, but not all, cases.

Of these, the *anodic* reaction of a freely corroding divalent metal can be written in simple form
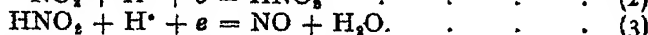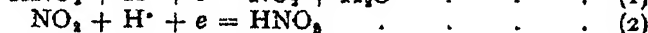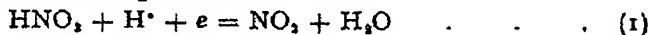
$$M + 2e = M^{\cdot\cdot}$$
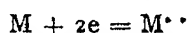
but the *cathodic* reaction requires detailed discussion.

Cathodic Behaviour of Nitric Acid.

There is evidence that at least two separate reactions can take place at a cathode surrounded by nitric acid, one leading to hydrogen and the other to nitrous acid. Actually this was known to Faraday,[4] but our detailed knowledge of the subject is due to Ellingham,[5] who showed that the potential-current density curves are different for the two reactions. Ellingham found that when an external E.M.F. is applied to a cell fitted with a platinum cathode,[6] hydrogen is evolved at first, and if the current density exceeds a certain critical value, hydrogen evolution will continue indefinitely. At current densities below this value, hydrogen evolution suddenly gives place to the formation of nitrous acid after a certain " transition time." The critical current density needed to ensure continued hydrogen evolution is much higher in concentrated acid than in dilute, but is further increased if appreciable amounts of nitrous acid are present at the outset ; conversely, if the nitric acid is freed from all traces of nitrous acid (and oxides of nitrogen) by drawing air through the solution (or, less efficiently, by adding urea [7]), the critical current density is greatly reduced, falling to very low values at concentrations below 6 N. The transition time can be greatly reduced by the presence of nitrous acid (*i.e.* the addition of potassium nitrite), and increased by removing traces of nitrous acid (and nitrogen oxides) in the manner just suggested. Evidently the reduction of nitric acid to nitrous acid is autocatalytic.

It might reasonably be supposed that the cathodic reduction of nitric acid would proceed in three steps as follows :—[8]

$$HNO_3 + H^{\cdot} + e = NO_2 + H_2O \qquad . \qquad . \qquad . \qquad (1)$$
$$NO_2 + H^{\cdot} + e = HNO_2 \qquad . \qquad . \qquad . \qquad (2)$$
$$HNO_2 + H^{\cdot} + e = NO + H_2O. \qquad . \qquad . \qquad (3)$$

[3] Hoar (*private communication*) writes : " The anodic and cathodic reactions can, I think, never occur simultaneously at the same points. They can occur simultaneously at adjacent points, or consecutively at the same point."

[4] Faraday, *Phil. Trans.*, 1834, 124, 96.
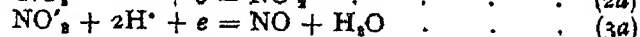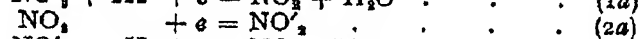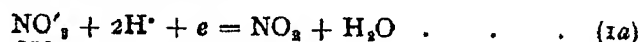
[5] Ellingham, *J. Chem. Soc.*, 1932, 1565.

[6] When the cathode is not platinum, the situation is more complicated, as shown by Thornhill (*Thesis*, London, 1935), who found several different potential-current density curves corresponding to the formation of different reduction products.

[7] Partington (*private communication*) has pointed out that hydrazine, or even hydrogen peroxide, are more efficient than urea for destroying nitrous acid.

[8] To simplify the equations, the hydrogen ion has been written H^{\cdot} instead of (H_3O)^{\cdot}. Ellingham (*private communication*) considers that in all cases hydrogen ions are first discharged, and that the hydrogen atoms then act as the reducing agent at each stage ; this still leaves the reduction of NO_3 as the change which involves fewest reacting particles, although the absolute numbers are altered.

If it is assumed that it is the ions which are concerned in the changes, the three equations may be rewritten thus :—

$$NO'_3 + 2H^{\bullet} + e = NO_2 + H_2O \qquad . \qquad . \qquad . \quad (1a)$$
$$NO_4 \qquad\qquad + e = NO'_2 \qquad . \qquad . \qquad . \quad (2a)$$
$$NO'_3 + 2H^{\bullet} + e = NO + H_2O \qquad . \qquad . \qquad . \quad (3a)$$

Of these six changes, (2a) involves only two reacting particles (including the electron) ; all the others involve three or four particles. Thus (2a) is the most likely to occur smoothly,[*] especially since, unlike most of the others, it does not involve the approach of a negatively charged particle to the negative pole—as pointed out by Hoar.[10] Now the nitrous acid formed in change (2) can easily regenerate NO_2 in *double the previous amount* through interaction with nitric acid,

$$HNO_2 + HNO_3 = 2NO_2 + H_2O \qquad . \qquad . \qquad . \quad (4)$$

—another change which involves two particles only, and which should therefore proceed easily. It now becomes evident that when *once a trace of nitrogen peroxide has been formed* (whether by equation (1) or otherwise), the reduction of nitric acid should proceed apace. Equations (2a) and (4) will proceed alternately, and *at each step the amounts of nitrogen peroxide and nitrous acid present will increase*, thus further stimulating the change.[11]

The small amount of nitrogen peroxide needed to start the auto-catalytic process may appear in various ways. Most samples of nitric acid contain nitrogen peroxide ; but probably if it were entirely absent, the compound would, at least in high concentrations of nitric acid, be produced slowly by equation (1).

Classification of Metals.

Most writers [12] have divided the metals into two classes according to their behaviour towards nitric acid :—

(A) **Highly Reactive Metals**, like magnesium, zinc and cadmium, which can liberate hydrogen from non-oxidising acids, yield either hydrogen or substances containing it when placed in nitric acid. On such metals, the anodic attack will in general be sufficiently rapid to produce a cathodic current density capable of maintaining the formation of hydrogen, although only in special cases, such as the reaction of magnesium with very dilute nitric acid, will hydrogen be obtained as such. In other cases the hydrogen, formed less rapidly, will react with the nitric acid to yield ammonia, hydroxylamine or hydrazine, and is not obtained in the free state.

(B) **Noble Metals** such as silver, mercury and copper, which cannot normally liberate hydrogen continuously at atmospheric pressure from non-oxidising acids,[13] do not yield hydrogen-rich bodies like ammonia or hydroxylamine with nitric acid. Instead of this the nitric acid is largely reduced to nitrous acid, the chief gas evolved being nitric oxide (NO). Here we are evidently experiencing the alternative cathodic reaction, and,

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[*] Ellingham (*private communication*) thinks that the ions (NO'_3) and (NO'_2). are not powerful oxidizing agents, although the molecule HNO_3 is ; for this reason, and also on account of the larger number of particles involved, equations (1a) and (3a) are less likely to occur readily than (1) and (3).

[10] Hoar, *private communication*.

[11] Joss (*J. Physic. Chem.*, 1926, 36, 1222) thinks that the " real depolarizer " is not NO_2, but its hydrate, $H_2N_2O_5$; evidence for the existence of $H_2N_2O_5$ is provided by Oddo (*Gazetta Chim. Ital.*, 1915, 45, I, 432) who has studied the depression of the freezing-point of nitrobenzene by NO_2 and H_2O.

[12] Divers, *J. Chem. Soc.*, 1883, 43, 443 ; Dhar, *J. Physic. Chem.*, 1925, 29, 142 ; Joss, *J. Physic. Chem.*, 1926, 30, 1222.

[13] Copper will evolve a certain amount of H_2 from boiling HCl, as well as from HBr and HI, doubtless because the formation of complex anions makes it behave as a more reactive metal.

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in view of its autocatalytic character, it is easy to understand why urea, which destroys nitrous acid and thus breaks the catalytic cycle, will repress the attack on the metal, as demonstrated by Veley,[14] and why the attack proceeds most readily at crannies between different pieces of metal where nitrous acid can accumulate. Stirring, which will dissipate the nitrous acid formed at the metallic surface, greatly slows down the action.

In this respect there is a strong contrast between the metals of classes (A) and (B). Hedges[15] states that the rotation of the metallic specimen, which diminishes the velocity of attack on Ag and Cu, stimulates that on Sn, Zn and Mg. Uchida and Sasaki[16] found that urea, which greatly slows down the dissolution of Cu, does not influence the attack upon Mg. The curious patterns, recalling Catharine-wheels, which appear on Cu discs whirled in HNO_3, are explained when it is remembered that the products of the attack catalyse the reaction. Such patterns were obtained by Urmánczy[17] on Cu and Ag, but not on Zn, as is easily understood. A single example of autocatalytic change can now be considered in greater detail.

Action of Nitric Acid on Copper.

When copper is introduced into nitric acid without artificial stirring, the reaction will at first be slow, unless nitrous acid is present in considerable quantities. As nitrous acid is formed by reaction (1), the autocatalytic cycle represented by reactions (2a) and (4) will lead to a steady increase in the amounts of nitrogen peroxide and nitrous acid, especially at the more stagnant parts of the surface, so that the rate of reaction will rapidly increase. Sooner or later, however, a steady state will be reached at which the formation of fresh nitrous acid is balanced by its destruction.

One possible method of destruction of nitrous acid is its reduction to nitric oxide according to reaction (3). In the steady state where the total nitrous acid present ceases to increase, the destruction of one molecule by reaction (3)

$$HNO_2 + H^{\cdot} + e = NO + H_2O$$
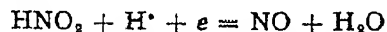
must balance the *net* production of one molecule by reactions (4) and (2a)

$$HNO_2 + HNO_3 = 2NO_2 + H_2O$$
$$2NO_2 + 2H^{\cdot} + 2e = 2HNO_2.$$
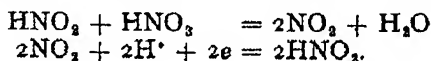
In this steady state the total change is obtained by adding these three equations, giving

$$HNO_3 + 3H^{\cdot} + 3e = NO + 2H_2O.$$
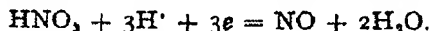
Alternatively, especially if the volume of liquid is small, so that the violent reaction appreciably raises the temperature, nitrous acid may be destroyed by decomposition to nitric oxide and nitric peroxide, which will then regenerate *half* the original quantity of nitrous acid. In this case the *net* loss of one molecule by the cycle

$$2HNO_2 = NO + NO_2 + H_2O$$
$$NO_2 + H^{\cdot} + e = HNO_2$$
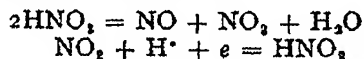
must balance the *net* gain of one molecule by the cycle

$$HNO_2 + HNO_3 = 2NO_2 + H_2O$$
$$2NO_2 + 2H^{\cdot} + 2e = 2HNO_2.$$
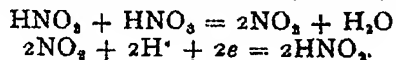
Adding these four equations together, we *again* arrive at the equation

$$HNO_3 + 3H^{\cdot} + 3e = NO + 2H_2O.$$
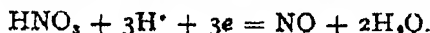
[14] Veley, *Proc. Roy. Soc.*, 1890, 46, 216.
[15] Hedges, *J. Chem. Soc.*, 1930, 561.
[16] Uchida and Sasaki, *J.S.C.I. Japan*, 1926, 29, 20B.
[17] Urmánczy, *Z. Anorg. Chem.*, 1938, 235, 363.

Evidently the same result is obtained whether the nitrous acid is lost by reduction, decomposition or both. This is the main cathodic reaction in the steady state, and clearly it must balance the electrical transfer of the anodic reaction
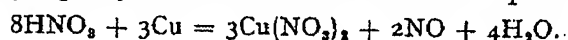
$$Cu = Cu^{..} + 2e.$$

The required electrical balance is obtained if the cathodic reaction is doubled, the anodic reaction trebled, and the two added together, so that the $6e$ transfer cancels out :—

$$2HNO_3 + 6H^. + 3Cu = 3Cu^{..} + 2NO + 4H_2O.$$
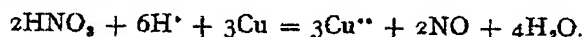
In order to preserve electrical neutrality, $6(NO_3')$ may be introduced on each side, and we have for the entire change

$$2HNO_3 + 6H^. + 6(NO_3') + 3Cu = 3Cu^{..} + 6NO'_3 + 2NO + 4H_2O$$
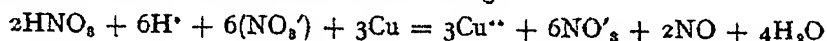
which is merely a partly ionised form of the textbook equation

$$8HNO_3 + 3Cu = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

Thus, without any special assumption, except that reactions involving few molecules are more probable than those involving several, it is possible to arrive at the equation given in the literature, and to explain why nitric oxide, although it may at first sight seem likely to be a minor product, is actually the main gaseous substance eliminated during the reaction. The more easily formed bodies will largely remain in solution, and thus re-enter the cycles of change.

It should be noticed, however, that this equation will only represent the change when once the steady state has been established, and even then it will be invalid if any of the other compounds involved are swept away from the metallic surface, for instance if much nitric peroxide passes off in the bubbles of nitric oxide, or if much nitrous acid is swept away far from the metallic surface into the body of the solution. The first complication may become important if the volume of liquid is small (leading to high temperatures), and especially at high acid concentrations, where nitric peroxide may become a main product ; the second will be most serious when the volume is large. Again, if the nitrous acid should, even in part, be decomposed according to the reaction

$$3HNO_2 = HNO_3 + 2NO + H_2O$$
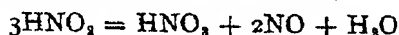
favoured by Abel, Schmid and Römer,[18] the autocatalytic chain would be broken, and the final result modified. A further complication may arise if the experiment is conducted in sunlight, which is thought by some to aid the reduction of nitric acid. Palit and Dhar [19] find that sunlight stimulates the action of nitric acid on copper.

Action of Nitric Acid on Iron.

Iron stands on the borderline between classes (A) and (B), and it would seem that both ammonia (characteristic of an A metal) and nitrous acid (characteristic of a B metal) are formed.[20] The ammonium nitrite produced readily decomposes, so that nitrogen is found among the gases evolved. A small amount of nitrous oxide (N_2O) may also be formed, possibly through the decomposition of ammonium nitrate. Whiteley and Hallimond [21] showed that above a certain concentration of nitric acid the combined production of ammonia plus nitrogen sharply declined ;

[18] Abel, Schmid and Römer, Z. physik. Chem. (A), 1930, 148, 337.

[19] Palit and Dhar, J. Physic. Chem., 1926, 30, 1125.

[20] Ellingham (private communication) considers that ammonia and nitrous acid are probably formed alternately.

[21] Whiteley and Hallimond, Carnegie Scholarship Memoirs (Iron and Steel Institute), 1918, 9, 1 ; 1925, 14, 163.

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this represents a sudden passage from A characteristics to B characteristics and corresponds to the sharp change in current-potential relations observed in Ellingham's work. It was found that plastic deformation of the iron increased the concentration at which the change of behaviour was observed, and this is easily understood, since the deformed iron, being richer in energy, will behave more like zinc and less like copper. The introduction of carbon into iron had the same effect—an important observation attributed by Whiteley to a strained condition of the iron present in pearlite ; this appears to be a very reasonable explanation.

Passivity of Iron.

Iron differs from many of the other metals in the fact that, although the corrosion velocity first increases with acid concentration, the velocity becomes variable at intermediate concentrations—as shown by the measurements of Portevin,[22] whilst at the highest concentrations nitric acid produces not corrosion but passivity. This is almost certainly due to the formation of an invisible film of ferric oxide. The presence of *some* film on iron immersed in nitric acid has been detected gravimetrically by Gulbransen,[23] who has followed the reduction of the film by hydrogen on a special microbalance, and optically by Tronstad and Borgmann.[24] There is no doubt that nitric acid is capable of producing an oxide film on iron under suitable circumstances. Benedicks and Sederholm,[25] treating iron in a mixture of alcohol, water and nitric acid, obtained visible films upon the surface. The author noticed that the gas evolved when diluted nitric acid acted upon partially immersed iron left interference tints where they had swept up over the dry metallic surface above the water-line. These relatively thick visible films were non-protective ; a protective material will, in general, stifle its own growth before it reaches visible thickness. But they do indicate that nitric acid, or some substance derived therefrom, can convert iron to its oxide, and it seems that, in the concentrated acid, the oxide film can check its own growth before reaching visible thickness.

The experiment just described rather suggests that nitrogen peroxide may be the agent which produces, by direct oxidation, the film responsible for passivity ; it is interesting to note that Varenne[26] rendered iron passive by immersion in liquid nitrogen peroxide under pressure.

It used to be asserted that passivity cannot be due to an oxide film, since, if such a film were formed, it would at once be dissolved by the acid. That this is untrue is proved by experiments on visible films. The author[27] has shown that a strip of electrolytic iron heated at one end so as to give the usual sequence of interference colours could be placed in concentrated nitric acid (sp. g. 1·4) without any change being observed in the colours after several hours. At the end of six days the oxide film had peeled off, indicating some attack along its base, but the films themselves were largely undissolved. When the same experiment was repeated with dilute acid (sp. g. 1·2) the iron was rapidly attacked at the untinted end, whilst the films at the tinted end were undermined and peeled off in ragged flakes, which remained undissolved after all the metal had disappeared. Evidently ferric oxide in film form is *not* readily attacked by nitric acid.

Resistance of Sesquioxides to Acids.—Actually oxides of the type M_2O_3 resist even non-oxidising acids far better than those of the type MO. The author[28] found that the destruction of the colours on heat-tinted

[22] Portevin, *Rev. Mét.*, 1929, 26, 615, 617.
[23] Gulbransen, *Trans. Electrochem. Soc.*, 1942, 82, 380.
[24] Tronstad and Borgmann, *Trans. Faraday Soc.*, 1934, 30, 349.
[25] Benedicks and Sederholm, *Z. physik. Chem. (A)*, 1928, 138, 123.
[26] Varenne, *Comptes rend.*, 1880, 90, 1001.
[27] Evans, *J. Chem. Soc.*, 1927, 1038.   [28] Evans, *ibid.*, 1930, 481.

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iron placed in dilute H_2SO_4 was merely due to cathodic reduction of the ferric oxide to the rapidly dissolving ferrous condition ; for if the tinted iron specimen was subjected to anodic treatment from the moment of its introduction into the acid, so as to avoid reduction, the colours remained undestroyed by the acid. If, however, the current was turned off for more than a few seconds, the colours vanished, evidently owing to the cathodic reduction of the film by means of the cells

<center>Iron | Acid | Ferric Oxide</center>

existing at discontinuities in the film. If, at the moment when the film had been destroyed at some areas and not at others, the current was turned on again, the anodic attack upon the iron caused the remaining film to be undermined and to peel off. When once it was out of contact with the metal it could remain in the acid for considerable periods without dissolving. Later the invisible film present on iron made passive by anodic treatment in sulphuric acid was isolated by anodic undermining in the same acid in an analogous way.[29] Here also the film was relatively stable towards acid when once out of contact with the metal.

It is worth noting that when heat-tinted iron has been subjected to anodic treatment in dilute H_2SO_4 for some time, the current may be turned off for a few seconds and then switched on again, without destruction of the colour films. During this short interruption, bubbles continue to rise from the anode, indicating that the surface of the metal is supersaturated with oxygen. Such a charge of excess oxygen will prevent the reduction of the ferric oxide to the ferrous condition by means of local cells, and thus preserve passivity. If the interruption of current is continued too long, the bubbles of oxygen cease to rise, showing that the supercharge has become exhausted ; in this case the colours are destroyed, and when the current is finally turned on again, it is employed, not in the production of oxygen, but on the dissolution of iron. It is clear that, to this limited extent, the old " oxygen-charge " theory of passivity is correct.

Whilst a charge of oxygen will serve to preserve passivity where otherwise it would disappear, a charge of hydrogen may serve to dispel passivity where otherwise it would be maintained. Schmidt[30] described an ex-, periment in which a thin sheet of iron divided a cell into two compartments. One compartment contained chromic acid and rendered the iron passive. Hydrogen was produced on the other side by cathodic action, and diffusing through the iron, rendered it active. Uhlig, Carr and Schneider[31] have described a rather similar experiment using stainless steel. In both cases the activity engendered by the diffusing hydrogen was probably due to the reduction of the oxide film, although the authors have preferred another explanation. There is no doubt that cathodic action can accelerate the thinning and destruction of the visible oxide films which produce interference colours on iron in dilute acids,[33] or even in weakly acid salt solutions, such as ammonium chloride. Miley's method[33] of estimating such films depends upon measuring the number of millicoulombs needed for their destruction, and comparison between the weight-loss and the number of millicoulombs indicate that the reduction proceeds as far as ferrous oxide, which immediately dissolves in the ammonium chloride solution, and not to metallic iron.

The author[34] found that the destruction of the visible films on heat-tinted iron on immersion in dilute sulphuric acid could be greatly slowed

[29] Evans, *Nature*, 1930, 126, 130. Confirmed by Müller, *Korrosion und Metallschutz*, 1932, 8, 255.
[30] Schmidt, *Trans. Faraday Soc.*, 1914, 9, 257.
[31] Uhlig, Carr and Schneider, *Trans. Electrochem. Soc.*, 1941, 79, 111.
[32] Evans, *Proc. Roy. Soc. (A)*, 1925, 107, 230.
[33] Miley and Evans, *J. Chem. Soc.*, 1937, 1298.
[34] Evans, *ibid.*, 1930, 481.

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down by the addition of an oxidising agent such as chromic acid. Such a body will prevent the reduction to the ferrous condition. Concentrated nitric acid, which is both acid and oxidising agent, should act like the chromic acid mixture and prevent the reduction. Thus, if it is admitted that nitric acid can convert iron even momentarily to the state of ferric oxide, this surface film will be neither dissolved directly, nor reduced to the rapidly dissolving ferrous condition, provided that the nitric acid is sufficiently concentrated. Clearly there will be come concentration below which the reduction, and consequent dissolution, will not be prevented, and this explains why dilute acid violently attacks iron, whereas concentrated acid maintains an oxide film, which will prevent attack upon the metal. At intermediate concentrations there is sometimes alternation between the active and passive states, whilst in other cases the decision between activity and passivity will depend upon conditions. A specimen which is passive may become violently attacked if touched momentarily by zinc, owing to the cathodic reduction of the film; conversely, iron which is suffering attack may often be made passive by contact with platinum.

Comparison between Behaviour of Iron and Copper.

It has been suggested above that nitrogen peroxide may be the substance which, by direct oxidation, leads to the protective film on iron placed in concentrated nitric acid, and this seems extremely probable, since when iron is brought into contact with the acid, there is at first some attack, which dies away, apparently as some substance accumulates near the surface; by whirling the iron in nitric acid Hedges [35] rendered passive iron active again.

Clearly, if nitrogen peroxide, which plays an essential part in the autocatalytic cycle on copper, is the cause of passivity on iron, then precisely those factors which retard corrosion under circumstances where passivity is unlikely, should, under conditions favourable for passivity, tend to maintain corrosion. This appears to be the case. Yamamoto [36] found that urea retarded the reaction on iron with dilute HNO_3 (doubtless by destroying nitrous acid and thus breaking the autocatalytic chain), but had the reverse effect in presence of concentrated nitric acid. It is interesting to note that he found an analogous state of affairs on Cu; although it retarded attack at concentrations below that limit. This suggests that even on Cu, notwithstanding the more rapid dissolution rate of its oxide, passivity may come into play under conditions where the formation of oxide is exceptionally rapid or its dissolution exceptionally slow. Partington [37] reports that fuming nitric acid (rich in nitrogen peroxide) renders Cu passive, although it is violently attacked when water is added. Hedges [38] has observed that at *low* temperatures ($-11°$ C.) ordinary HNO_3 renders Cu passive owing to the production of a visible, dark grey film; on warming, sudden violent dissolution occurred at 40° C. He points out that the passivity of Cu is not so permanent as that of Fe; if the Cu be removed from the acid, washed with water and replaced, it dissolves with vigour, the reason being that cupric oxide is dissolved by dilute HNO_3 at ordinary temperature, whilst ferric oxide is not.

In another respect the reaction of iron differs from that of most other metals. If any nitric oxide (NO) is formed, either by thermal decomposition of nitrous acid, or by its reduction through reaction (3), it will be retained as a nitroso-compound by the ferrous salts formed in the anodic reaction, instead of escaping in bubbles; it can then be reoxidised to

[35] Hedges, *J. Chem. Soc.*, 1928, 971.
[36] Yamamoto, *Bull. Inst. Phys. Chem. Res. (Tokyo)*, 1936, 15, 981, 1209; 1937, 16, 59; *Chem. Abst.*, 1937, 6593.
[37] Partington, *private communication*.
[38] Hedges, *J. Chem. Soc.*, 1928, 975.

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nitric peroxide (NO_2). A new catalytic chain thus becomes, on paper, possible, in which the compound $Fe(NO)(NO_3)_2$, which has been identified by its absorption spectrum on reacting iron by Karschulin,[39] plays an essential part. It seems, however, more likely that the main autocatalysis is of another character.

Mechanism of the Transmission of Activity on Iron wetted by Nitric Acid of Borderline Concentration.

Any attack upon iron which expels oxides of nitrogen will increase the ratio of H_2O to N_2O_5 in the residual liquid. Since, over a certain range of concentration, the danger of corrosion increases as acid concentration diminishes, it is clear that, when once attack has set in, it will become more and more rapid, provided that the products are not dissipated by stirring ; the rise of temperature will also help. This is probably the reason why the attack upon iron by nitric acid at the borderline between the ranges which produce corrosion and passivity respectively is so much more vigorous at crannies, where the products of attack will be retained, than elsewhere. We have here a third type of autocatalytic chain, with water playing the dominant rôle. It may possibly supply the reason why attack proceeds so readily at the water-line, where the meniscus provides an inaccessible cranny, as pointed out by Schikorr.[40] But two alternative causes of water-line attack may be found (1) in the ready escape of nitrogen peroxide from this zone, and (2) in the possibility of the oxide film adhering to the acid/air interface instead of to the metal, and thus failing locally to protect.[41]

Many examples are available of the special attack of nitric acid on iron at the water-line. The author[42] wetted a strip of iron with nitric acid (sp. g. 1·4), allowed it to drain until the reaction had started at one point, and then plunged it into HNO_3 with sufficient motion to dissipate the corrosion products, whereupon the transmission ceased and the whole became quiescent. When, however, another reacting strip was introduced gently into the acid, so as to allow the corrosion products to accumulate, the reaction became violent at the water-line, and the strip was here eaten right through within a minute ; the lower part, cut off completely by the attack at the water-line, dropped to the bottom of the vessel and there remained unattacked. In some of his experiments Hedges[43] found that if a piece of iron foil was gently dropped into 7 to 14 % HNO_3 (by volume), with its flat face on to the liquid surface, it was dissolved with great vigour, whereas a similar piece thrown edgewise through the surface escaped attack.

Many of the experiments described by Heathcote,[44] Lillie,[45] and others on the transmission of attack along iron wires or rods may be suitably explained by the fact that the reaction at one point alters the ratio of H_2O to N_2O_5 in a sense favourable to attack at neighbouring points. The fact that such transmission proceeds downwards more readily than upwards suggests the simple autocatalytic explanation. On the other hand, electro-chemical action may play a part. Anodic attack upon metal at one point will cause corresponding cathodic action upon the points around, which will replace passivity by activity.

The view that water is the cause of the autocatalytic breakdown of passivity receives support from the well-known fact that in mixtures of

[39] Karschulin, *Z. Elektrochem.*, 1935, 41, 664.

[40] Schikorr, *private communication.*

[41] Thornhill regards this last explanation as improbable and the author is inclined to agree.

[42] Evans, *J. Chem. Soc.*, 1927, 1037.

[43] Hedges, *ibid.*, 1928, 970.

[44] Heathcote, *J.S.C.I.*, 1907, 26, 899 ; esp. p. 908.

[45] Lillie, *J. Gen. Physiology*, 1920, 3, 107, 129.

nitric acid and sulphuric acid, passivity is persistent and reliable, so that mixed acid can be handled safely in steel, whilst in pure nitric acid the passivity is liable to break down unexpectedly, *e.g.* on abrasion.

Materials Resistant to Dilute Nitric Acid.

If it is admitted that the destruction of the oxide film set up by nitric acid is due to reduction rather than to direct dissolution, it is clear that metals which exist only in the trivalent condition should resist nitric acid better than iron. This is found to be the case. Aluminium is only slowly attacked by nitric acid sufficiently dilute to act with vigour on iron.[46] Chromium represents an intermediate case; it forms divalent salts, but they are far less stable than the corresponding ferrous salts. Chromium is less attacked than iron by nitric acid, but more attacked by hydrochloric acid. It is reasonable to expect that the introduction of a limited quantity of chromium into iron would yield with nitric acid an oxide containing sufficient chromium to stabilise the M_2O_3 condition, and thus resist nitric acid of a concentration sufficient to attack vigorously ordinary iron. This proves to be the case. Stainless steel is far more resistant to dilute nitric acid than is iron, although, in the absence of a third metal, it is more rapidly attacked by hydrochloric acid. In one class of acid-resistant alloys (also containing silicon) discussed by Rabald,[47] chromium is in part replaced by aluminium, but there are practical limitations to this replacement on mechanical and other grounds.

Other Views.

A special theory of the passivity of stainless steel has recently been advanced by Uhlig and Wulff.[48] According to this view, the iron atoms share their electrons with the chromium atoms, and lose the power of reacting; thus an explanation of the fact that the passivity sets in at about 12 % of chromium is put forward. Apart from a possible difficulty in reconciling this view with modern physical opinion, it does not appear to explain the chemical facts. If the iron atoms lose their power of combining at 12 %, the stainless steels should be relatively inert towards all reagents. Actually they are more readily attacked by hydrochloric acid than ordinary iron. Even pure water containing oxygen acts on film-free stainless steel at the outset as quickly as on ordinary iron, as shown in the researches of Forrest, Roetheli and Brown;[49] but whereas the oxidation of the ordinary iron continues indefinitely, that of the stainless steel slows down as soon as an oxide film is formed. Probably the ordinary iron passes into solution as ferrous hydroxide, which is precipitated as ferric hydroxide at an appreciable distance from the surface, whereas in the case of the chromium alloy, the sesquioxide or its hydrate is formed directly, and thus protects the metal, the divalent condition being less stable. Finally, it should be pointed out that the immune character of stainless steel does not necessarily set in at 12 %. To withstand high-temperature steam, less Cr is needed; since the formation of a non-porous, adherent and protective skin commences at about 7 % Cr.[50] There is little doubt that the influence of Cr in raising the resistance of iron towards certain reagents is due to the improvement of the oxide film formed.

[46] Monypenny (*Stainless Iron and Steel*, 1931, p. 349 (Chapman and Hall)), states that the corrosion rate of 0·16 % carbon steel in nitric acid of sp.g. 1·20 (33 %) is 12,500 grams per sq. metre per hour, which is equivalent to 1·5 mm. per hour. Inglis (*private communication*) states that the attack upon aluminium by nitric acid becomes most serious at about 30 % concentration, when it is 2·7 mm. per year.   [47] Rabald, *Chem. Fabrik*, 1935, 8, 29.
  [48] Uhlig and Wulff, *Trans. Amer. Inst. Min. Met. Eng.*, 1939, 135, 494 ; 1940, 140, 387. *Cf.* Ryan and Herbert, *Trans. Electrochem. Soc.*, 1940, 77, 427.
  [49] Forrest, Roetheli and Brown, *Ind. Eng. Chem.*, 1930, 22, 1197.
  [50] Solberg, Hawkins and Potter, *Trans. Amer. Soc. Mech. Eng.*, 1942, 64, 303.

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Some of Uhlig's suggestions may have significance in special cases. Where the presence of hydrogen in a lattice perceptibly increases the distance between atoms, the separation of these atoms during the process may be facilitated. According to Wever and Pfarr,[51] hydrogen does cause a distention of the lattice in ordinary steel, but the increase of parameter is very small. Hydrogen may, however, cause the breakdown of passivity in another way. The sudden formation of molecular hydrogen under pressure in the interior of iron charged with hydrogen can lead to serious embrittlement and blistering ; the internal evolution on a much smaller scale might easily cause the local breakdown of an oxide skin, and consequently failure of passivity. But any action of hydrogen in distending the metal is probably less important as a cause of the breakdown of passivity than its power to reduce an oxide film.

Summary.

The principal facts regarding the behaviour of metals towards nitric acid can be explained without special assumptions other than that (1) those equations are most probable which involve fewest molecules, (2) oxides of type M_2O_3 are dissolved far less quickly than those of type MO, for which there is experimental evidence. The first assumption leads to the view that the attack on relatively noble metals like copper will be *autocatalytic*, since the two most probable equations constitute a cycle at which the concentration of nitrous acid is *doubled at each stage*. This in turn explains the well-known effect of stirring and of additions of urea. Autocatalysis is absent on metals like zinc which yield hydrogen-rich products. The second assumption explains why iron, although violently attacked by dilute nitric acid, is rendered passive by concentrated acid. The breakdown of passivity is connected, not with direct dissolution of the sesquioxide, but with reduction to the rapidly dissolving divalent condition ; it can be avoided by suitable anodic treatment, which prevents the destructive transformation, as is made apparent by experiments on iron covered with visible films of interference colour thickness ; such films—when out of contact with metal—resist dissolution by acid. This argument leads to an explanation of the fact that nitric acid sufficiently dilute to act violently on iron, has only a slow action on aluminium where divalent compounds are absent, or on iron containing chromium—a metal forming only unstable divalent compounds.

[51] Wever and Pfarr, *Mitt. Kaiser-Wilhelm Inst. Eisenforschung.*, 1933, 15, 147.